

08/693, 789

(FILE 'HOME' ENTERED AT 12:14:19 ON 10 OCT 1997)

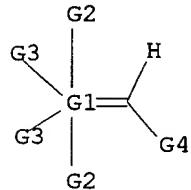
FILE 'REGISTRY' ENTERED AT 12:14:25 ON 10 OCT 1997

L1 SCREEN 1977  
L2 SCREEN 2127  
L3 SCREEN 2049  
L4 STRUCTURE uploaded  
L5 QUE L4 AND L3 NOT L1 NOT L2

=> d 15

'L5' HAS NO ANSWERS

L1 SCR 1977  
L2 SCR 2127  
L3 SCR 2049  
L4 STR



G1 Os,Ru

G2 H,O,S,N,P,As,Sb

G3 X,Cb,Ak,H,Ph,o-C6H4,OH,SH,MeO,EtO,n-PrO,PhO

G4 H,Me,Et,n-Pr,i-Pr,n-Bu,i-Bu,s-Bu,t-Bu,Ph,o-C6H4,m-C6H4,p-C6H4

Structure attributes must be viewed using STN Express query preparation.

L5 QUE L4 AND L3 NOT L1 NOT L2

=> s 15

SAMPLE SEARCH INITIATED 12:15:36  
SAMPLE SCREEN SEARCH COMPLETED - 8669 TO ITERATE  
11.5% PROCESSED 1000 ITERATIONS 2 ANSWERS  
INCOMPLETE SEARCH (SYSTEM LIMIT EXCEEDED)  
SEARCH TIME: 00.00.02

FULL FILE PROJECTIONS: ONLINE \*\*INCOMPLETE\*\*  
BATCH \*\*COMPLETE\*\*  
PROJECTED ITERATIONS: 167822 TO 178938  
PROJECTED ANSWERS: 97 TO 595

L6 2 SEA SSS SAM L4 AND L3 NOT L1 NOT L2

=> s 15 full

FULL SEARCH INITIATED 12:15:52  
FULL SCREEN SEARCH COMPLETED - 173433 TO ITERATE  
28.2% PROCESSED 48893 ITERATIONS ( 1 INCOMPLETE) 61 ANSWERS  
49.8% PROCESSED 86364 ITERATIONS ( 2 INCOMPLETE) 131 ANSWERS

57.0% PROCESSED 98921 ITERATIONS ( 2 INCOMPLETE) 136 ANSWERS  
57.7% PROCESSED 100000 ITERATIONS ( 2 INCOMPLETE) 136 ANSWERS  
INCOMPLETE SEARCH (SYSTEM LIMIT EXCEEDED)  
SEARCH TIME: 00.01.04

FULL FILE PROJECTIONS: ONLINE \*\*INCOMPLETE\*\*  
BATCH \*\*COMPLETE\*\*  
PROJECTED ITERATIONS: 173433 TO 173433  
PROJECTED ANSWERS: 189 TO 281

L7 136 SEA SSS FUL L4 AND L3 NOT L1 NOT L2

=> fil ca

COST IN U.S. DOLLARS	SINCE FILE ENTRY	TOTAL SESSION
FULL ESTIMATED COST	111.28	111.43

FILE 'CA' ENTERED AT 12:17:04 ON 10 OCT 1997  
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FILE COVERS 1967 - 7 Oct 1997 (971007/ED) VOL 127 ISS 15

This file contains CAS Registry Numbers for easy and accurate substance identification.

=> s 17

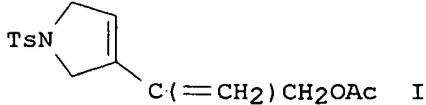
L8 95 L7

=> s 18 and py<=1994

12128212 PY<=1994  
L9 13 L8 AND PY<=1994

=> d 1-13 bib abs

L9 ANSWER 1 OF 13 CA COPYRIGHT 1997 ACS  
AN 122:160379 CA  
TI Ruthenium catalyzed enyne metathesis  
AU Kinoshita, Atsushi; Mori, Miwako  
CS Fac. Pharm. Sci., Hokkaido Univ., Sapporo, 060, Japan  
SO Synlett (1994), (12), 1020-22  
CODEN: SYNLES; ISSN: 0936-5214  
DT Journal  
LA English  
OS CASREACT 122:160379  
GI



AB Enyne metathesis reaction was realized utilizing a ruthenium catalyst reported by Grubbs (1993). Thus, five-, six- and seven-membered heterocycles, e.g. I, were synthesized from enynes, e.g. CH<sub>2</sub>:CHCH<sub>2</sub>N(Ts)CH<sub>2</sub>C.tpbond.CCH<sub>2</sub>OAc, in good yields.

L9 ANSWER 2 OF 13 CA COPYRIGHT 1997 ACS

AN 122:81462 CA

TI Catalytic Ring Closing Metathesis of Dienynes: Construction of Fused Bicyclic Rings

AU Kim, Soong-Hoon; Bowden, Ned; Grubbs, Robert H.

CS Arnold and Mabel Beckman Laboratory of Chemical Synthesis, California Institute of Technology, Pasadena, CA, 91125, USA

SO J. Am. Chem. Soc. (1994), 116(23), 10801-2

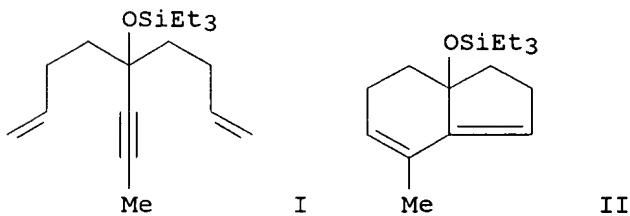
CODEN: JACSAT; ISSN: 0002-7863

DT Journal

LA English

OS CASREACT 122:81462; CJACS-IMAGE; CJACS

GI



AB Ru carbene Cl<sub>2</sub>(PCy<sub>3</sub>)<sub>2</sub>Ru:CHCH:CPh<sub>2</sub> mediates the efficient conversion of acyclic dienynes, e.g., I, to fused bicyclic [n.m.0] rings contg. 5, 6 and 7 membered rings, e.g., II. With unsym. dienynes, the olefin substitution regulates the selective formation of a single fused bicyclic ring. These observations further expand the scope of catalytic ring closing metathesis for the construction of complex org. compds.

L9 ANSWER 3 OF 13 CA COPYRIGHT 1997 ACS

AN 122:10702 CA

TI Ring-opening metathesis polymerization catalysts

AU Grubbs, Robert H.; Hillmyer, Marc; Benedicto, Alto; Wu, Zhe

CS Div. Chem. Chem. Eng., California Inst. Technol., Pasadena, CA, 91125, USA

SO Polym. Prepr. (Am. Chem. Soc., Div. Polym. Chem.) (1994), 35(1), 688

CODEN: ACPPAY; ISSN: 0032-3934

DT Journal; General Review

LA English

AB A review with 6 refs. describing the effectiveness of ruthenium complexes in ring-opening metathesis polymn. of various cyclic compds.

L9 ANSWER 4 OF 13 CA COPYRIGHT 1997 ACS

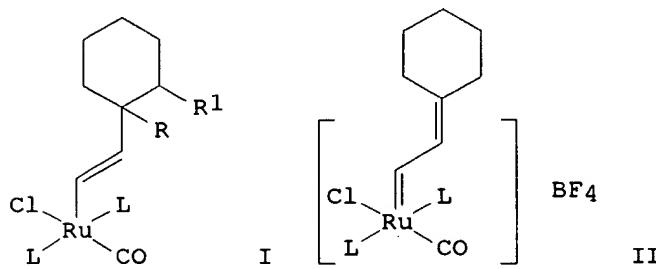
AN 121:280836 CA

TI Reactions of RuHCl(CO)(PiPr<sub>3</sub>)<sub>2</sub> with Alkyn-1-ols: Synthesis of Ruthenium(II) Hydroxyvinyl and Vinylcarbene Complexes

AU Esteruelas, Miguel A.; Lahoz, Fernando J.; Onate, Enrique; Oro, Luis A.; Zeier, Bernd

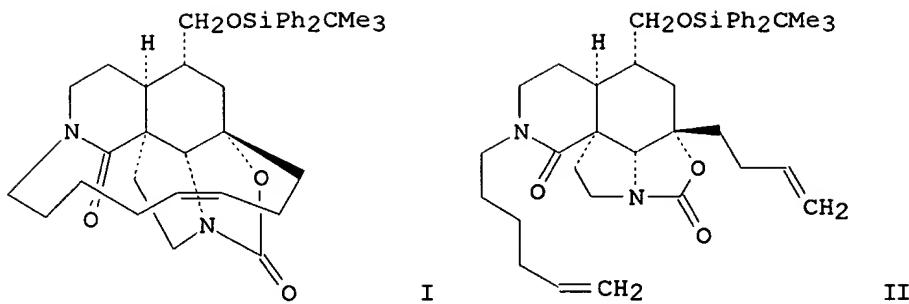
CS Instituto de Ciencia de Materiales de Aragon, Universidad de Zaragoza, Zaragoza, 50009, Spain

SO Organometallics (1994), 13(11), 4258-65  
CODEN: ORGND7; ISSN: 0276-7333  
DT Journal  
LA English  
OS CASREACT 121:280836; CJACS-IMAGE; CJACS  
GI



AB The monohydrido complex  $\text{RuHCl}(\text{CO})(\text{L})_2$  (1,  $\text{L} = (\text{Me}_2\text{CH})_3\text{P}$  throughout this abstr.) reacts with  $\text{HC}(\text{tplbnd.CC}(\text{OH})\text{R}_1\text{R}_2)$  to give the hydroxyvinyl compds.  $\text{RuCl}\{(\text{E})\text{-CH:CHC}(\text{OH})\text{R}_1\text{R}_2\}(\text{CO})(\text{L})_2$  ( $\text{R}_1 = \text{R}_2 = \text{H}$  (2);  $\text{R}_1 = \text{H}$ ,  $\text{R}_2 = \text{Ph}$  (3);  $\text{R}_1 = \text{R}_2 = \text{Ph}$  (4)), which by reaction with  $\text{HBF}_4$  afford  $[\text{RuCl}(:\text{CHCH:CR}_1\text{R}_2)(\text{CO})(\text{L})_2]\text{BF}_4$  ( $\text{R}_1 = \text{H}$ ,  $\text{R}_2 = \text{Ph}$  (5);  $\text{R}_1 = \text{R}_2 = \text{Ph}$  (6)). The former cationic compds. react with  $\text{NaCl}$  to give  $\text{RuCl}_2(:\text{CHCH:CR}_1\text{R}_2)(\text{CO})(\text{L})_2$  ( $\text{R}_1 = \text{H}$ ,  $\text{R}_2 = \text{Ph}$  (7);  $\text{R}_1 = \text{R}_2 = \text{Ph}$  (8)). The mol. structure of 6 was detd. by x-ray crystallog. The geometry around the ruthenium atom can be described as a square pyramid with the alkylidene ligand located in the apex. The base is formed by the carbonyl ligand and the chlorine atom mutually trans disposed, with two triisopropylphosphine groups. The complexes 2-4 react with  $\text{CO}$  to give the cis-dicarbonyl compds.  $\text{RuCl}\{(\text{E})\text{-CH:CHC}(\text{OH})\text{R}_1\text{R}_2\}(\text{CO})_2(\text{L})_2$  ( $\text{R}_1 = \text{R}_2 = \text{H}$  (9);  $\text{R}_1 = \text{H}$ ,  $\text{R}_2 = \text{Ph}$  (10);  $\text{R}_1 = \text{R}_2 = \text{Ph}$  (11)). The reaction of 1 with 1-ethynyl-1-cyclohexanol affords ruthenium complex I ( $\text{R} = \text{H}$ ,  $\text{R}_1 = \text{OH}$ ), which after 4 days in toluene at 60.degree. gives I ( $\text{RR}_1 = \text{bond}$ ). The reaction of I ( $\text{RR}_1 = \text{bond}$ ) with  $\text{HBF}_4$  leads to vinylcarbene complex II, which can also be obtained from the reaction of I ( $\text{R} = \text{H}$ ,  $\text{R}_1 = \text{OH}$ ) with  $\text{HBF}_4$ .

L9 ANSWER 5 OF 13 CA COPYRIGHT 1997 ACS  
AN 121:109359 CA  
TI The first synthesis of the ABCD ring system of manzamine A.  
Construction of the macrocyclic ring D  
AU Borer, Bennett C.; Deerenberg, Sirik; Bieraeugel, Hans; Pandit,  
Upendra K.  
CS Lab. Org. Chem., Univ. Amsterdam, Amsterdam, 1018 WS, Neth.  
SO Tetrahedron Lett. (1994), 35(19), 3191-4  
CODEN: TELEAY; ISSN: 0040-4039  
DT Journal  
LA English  
OS CASREACT 121:109359  
GI



AB The synthesis of the ABCD ring system I of manzamine A has been achieved using the olefin metathesis cyclization reaction of II for the crucial macrocyclic ring D formation step.

L9 ANSWER 6 OF 13 CA COPYRIGHT 1997 ACS

AN 121:35835 CA

TI Reactions of OsHCl(CO)(PiPr<sub>3</sub>)<sub>2</sub> with Alkyn-1-ols: Synthesis of (Vinylcarbene)osmium(II) Complexes

AU Esteruelas, Miguel A.; Lahoz, Fernando J.; Onate, Enrique; Oro, Luis A.; Zeier, Bernd

CS Instituto de Ciencia de Materiales de Aragon, Universidad de Zaragoza, Zaragoza, 50009, Spain

SO Organometallics (1994), 13(5), 1662-8  
CODEN: ORGND7; ISSN: 0276-7333

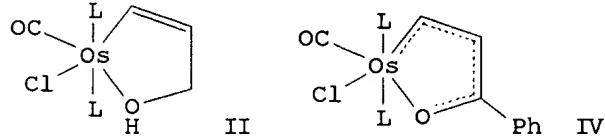
DT Journal

## LA English

OS CASREAC

GT

1



AB The monohydride complex  $\text{OsHCl}(\text{CO})\text{L}_2$  [I,  $\text{L} = \text{P}(\text{CHMe}_2)_3$  through out this abstr.] reacts with 2-propyn-1-ol to give the vinyl compd. II. The reaction of I with 1-phenyl-2-propyn-1-ol leads to a mixt. of products, from which the complexes  $\text{OsCl}_2(:\text{CHCH:CHPh})(\text{CO})\text{L}_2$  (III) and heterocycle IV were sepd. The mol. structures of complexes III and IV were detd. by x-ray crystallog. The coordination around the osmium atom in III can be described as a distorted octahedron with the two triisopropylphosphine ligands occupying trans positions; the perpendicular plane is defined by the vinylcarbene and a carbonyl ligand, mutually cis disposed, and by two chloride atoms. The osmium coordination environment in IV can also be rationalized as a distorted octahedron with the two phosphine ligands disposed mutually trans. The remaining coordination sites of the octahedron are occupied by the carbonyl ligand, the chloride atom, and the chelate  $\text{CHCH}(\text{O})\text{Ph}$  ligand. The reaction of I with 1,1-diphenyl-2-propyn-1-ol also leads to a mixt. of products, from which the complex  $\text{OsCl}_2(:\text{CHCH:CPh}_2)(\text{CO})\text{L}_2$  was isolated and characterized.

L9 ANSWER 7 OF 13 CA COPYRIGHT 1997 ACS

AN 120:299528 CA

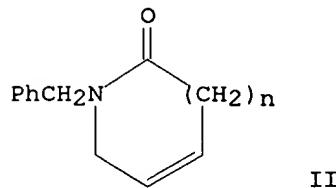
TI Ruthenium and osmium metal carbene complexes for cycloolefin metathesis polymerization

IN Grubbs, Robert Howard; Johnson, Lynda Kaye; Nguyen, Sonbinh Thebaud  
PA du Pont de Nemours, E. I., and Co., USA; California Institute of  
Technology  
SO PCT Int. Appl., 43 pp.  
CODEN: PIXXD2  
PI WO 9320111 A2 **931014**  
DS W: JP, KR  
RW: AT, BE, CH, DE, DK, ES, FR, GB, GR, IE, IT, LU, MC, NL, PT, SE  
AI WO 93-US3425 930405  
PRAI US 92-863606 920403  
DT Patent  
LA English  
OS MARPAT 120:299528  
AB The title compds. bear Os or Ru atoms in the +2 oxidn. state and are  
stable in the presence of protic solvents, and are useful as high  
activity ring-opening metathetic catalysts for polymn. of  
cycloolefins. A catalyst was prep'd. by reaction of  
tetrakis(triphenylphosphine)ruthenium dichloride and  
3,3-diphenylcyclopropene and was used to polymerize norbornene.

L9 ANSWER 8 OF 13 CA COPYRIGHT 1997 ACS  
AN 120:107300 CA  
TI Conformation of d6 carbene complexes in an asymmetric octahedral  
field. II  
AU Maouche, Boubeker; Volatron, Francois; Jean, Yves  
CS Inst. Chim., Univ. Sci. Technol. Houari Boumediene, Algiers,  
Algeria  
SO New J. Chem. (1993), 17(7), 449-53  
CODEN: NJCHE5; ISSN: 1144-0546  
DT Journal  
LA French  
AB The conformation of d6 carbene complexes in asym. octahedral ligand  
fields  $[M(PH_3)_2(Cl)_2(X)(CY_2)$ , X = CO, Cl-; Y = H, Cl] is studied by  
means of Extended Hueckel calcns. First, model complexes are  
studied in order to analyze the relative strength of back donation  
and steric repulsion, depending on the substitution pattern of the  
metal and the carbene. For X = Cl-, back donation and steric  
effects work in opposite directions. In the unsubstituted case (Y =  
H), the two factors almost cancel and no marked preference is found.  
For the deactivated carbene (Y = Cl), steric effects dominate and  
the carbene plane lies between the C-M-Cl and C-M-PH<sub>3</sub> planes, and  
closer to the former. For X = CO, the back donation interaction and  
the steric effects favor (weakly and strongly, resp.) the  
conformation with the carbene coplanar with the CO-M-Cl linkage.  
Calcns. on models for exptl. complexes confirm these trends and are  
in agreement with available exptl. data.

L9 ANSWER 9 OF 13 CA COPYRIGHT 1997 ACS  
AN 120:9085 CA  
TI Syntheses and activities of new single-component, ruthenium-based  
olefin metathesis catalysts  
AU Nguyen, SonBinh T.; Grubbs, Robert H.; Ziller, Joseph W.  
CS Div. Chem. Chem. Eng., California Inst. Technol., Pasadena, CA,  
91125, USA  
SO J. Am. Chem. Soc. (1993), 115(21), 9858-9  
CODEN: JACSAT; ISSN: 0002-7863  
DT Journal  
LA English  
OS CJACS-IMAGE; CJACS  
AB  $(\text{Iso-Pr}_3\text{P})_2\text{Cl}_2\text{Ru:CHCH:CPh}_2$  (I) is prep'd. in good yield from  
 $(\text{Ph}_3\text{P})_2\text{Cl}_2\text{Ru:CHCH:CPh}_2$  (II). While I shares the stability of II in  
the presence of aq./protic solvents, it is several orders of  
magnitude more active as an olefin metathesis catalyst. In contrast  
to II, I catalyzes the metathesis of cis-2-pentene. I also  
catalyzes the ring-opening metathesis polymn. of norbornene.

L9 ANSWER 10 OF 13 CA COPYRIGHT 1997 ACS  
 AN 119:270983 CA  
 TI Catalytic ring-closing metathesis of functionalized dienes by a ruthenium carbene complex  
 AU Fu, Gregory C.; Nguyen, SonBinh T.; Grubbs, Robert H.  
 CS Arnold and Mabel Beckman Lab. Chem. Synth., California Inst. Technol., Pasadena, CA, 91125, USA  
 SO J. Am. Chem. Soc. (1993), 115(21), 9856-7  
 CODEN: JACSAT; ISSN: 0002-7863  
 DT Journal  
 LA English  
 OS CASREACT 119:270983; CJACS-IMAGE; CJACS  
 GI



AB Ruthenium carbene Ph<sub>2</sub>C:CHC:Ru(PCy<sub>3</sub>)<sub>2</sub>Cl<sub>2</sub> (I; Cy = cyclohexyl) catalyzes the cyclization of a wide range of functionalized dienes, affording five-, six-, and seven-membered heterocycles and carbocycles in good yield. Thus, treatment of N-allylalkenylamides H<sub>2</sub>C:CH(CH<sub>2</sub>)<sub>n</sub>CON(CH<sub>2</sub>Ph)CH<sub>2</sub>CH:CH<sub>2</sub> (n = 0-2) with 2-4 mol% I at room temp. in benzene gave unsatd. lactams II in 78-91% yields. The ruthenium-catalyzed metathesis reaction is significantly less sensitive than is the corresponding molybdenum-catalyzed process; it is tolerant of carboxylic acids, alcs., aldehydes, and amine salts, and it can be effected in air.

L9 ANSWER 11 OF 13 CA COPYRIGHT 1997 ACS  
 AN 119:117888 CA  
 TI Living ring-opening metathesis polymerization of bicyclo[3.2.0]heptene catalyzed by a ruthenium alkylidene complex  
 AU Wu, Zhe; Benedicto, Alto D.; Grubbs, Robert H.  
 CS Arnold and Mabel Beckman Lab. Chem. Synth., California Inst. Technol., Pasadena, CA, 91125, USA  
 SO Macromolecules (1993), 26(18), 4975-7  
 CODEN: MAMOBX; ISSN: 0024-9297  
 DT Journal  
 LA English  
 OS CJACS-IMAGE; CJACS  
 AB The complex (PPh<sub>3</sub>)<sub>2</sub>(Cl)<sub>2</sub>Ru(:CH-CH:CPh<sub>2</sub>) catalyzes the living ring-opening metathesis polymn. of bicyclo[3.2.0]heptene. The starting alkylidene initiates completely during the polymn. and the propagating alkylidenes are stable throughout the polymn. The polymer obtained has a narrow polydispersity of 1.2, and the mol. wts. are proportional to the ratio of monomer/catalyst. Diblock and triblock copolymers can be prep'd. by the sequential addn. of either bicyclo[3.2.0]heptene or norbornene.

L9 ANSWER 12 OF 13 CA COPYRIGHT 1997 ACS  
 AN 116:194941 CA  
 TI Ring-opening metathesis polymerization (ROMP) of norbornene by a Group VIII carbene complex in protic media  
 AU Nguyen, SonBinh T.; Johnson, Lynda K.; Grubbs, Robert H.; Ziller, Joseph W.  
 CS Div. Chem. Chem. Eng., California Inst. Technol., Pasadena, CA,

91125, USA  
SO J. Am. Chem. Soc. (1992), 114(10), 3974-5  
CODEN: JACSAT; ISSN: 0002-7863  
DT Journal  
LA English  
OS CJACS-IMAGE; CJACS  
AB The complex  $(\text{Ph}_3\text{P})_2\text{Cl}_2\text{Ru}=\text{CHCH}=\text{CPH}_2$  (I) is prep'd. in quant. yield by the reaction of 3,3-diphenylcyclopropene with either  $\text{RuCl}_2(\text{PPh}_3)_3$  or  $\text{RuCl}_2(\text{PPh}_3)_4$ . Complex I polymerizes norbornene in org. media both in the absence and presence of protic/aq. solvents. In both solvent systems, a stable propagating carbene species can be obsd. throughout the course of the polymn., as was previously found with Ti, Ta, W, Mo, and Rh complexes. These observations establish metal carbene species as viable intermediates in the ROMP of bicyclic olefins catalyzed by classical Ru coordination complexes in protic solvents.

L9 ANSWER 13 OF 13 CA COPYRIGHT 1997 ACS  
AN 114:16467 CA  
TI Behavior of di-.mu.-acetato-tetracarbonylbis(tributylphosphine)diruthenium in the presence of hydrogen: synthesis and x-ray structure of polynuclear ruthenium carbonyl hydrides containing an encapsulated phosphide ligand  
AU Frediani, Piero; Bianchi, Mario; Salvini, Antonella; Piacenti, Franco; Ianelli, Sandra; Nardelli, Mario  
CS Dip. Chim. Org., Univ. Firenze, Florence, I-50121, Italy  
SO J. Chem. Soc., Dalton Trans. (1990), (5), 1705-16  
CODEN: JCDTBI; ISSN: 0300-9246  
DT Journal  
LA English  
OS CJRSC  
AB  $[\text{Ru}_2(\text{CO})_4(\text{.mu.-OAc-O',})_2(\text{PBu}_3)_2$  under H (170 atm), at 140-200.degree., undergoes rearrangements. Several phosphine- and phosphide-substituted Ru carbonyl hydrides are formed. Among them,  $[\text{Ru}_3(\text{.mu.-H})_2(\text{CO})_7(\text{.mu.3-PBu})(\text{PBu}_3)_2]$  (I),  $[\text{Ru}_6(\text{.mu.-H})_6(\text{.mu.-CO})(\text{CO})_{12}(\text{.mu.-PBu}_2)(\text{PBu}_3)_2(\text{.mu.6-P})]$  (II), and  $[\text{Ru}_7(\text{.mu.-H})_8(\text{CO})_{12}(\text{.mu.3-PBu})(\text{.mu.-PBu}_2)(\text{PBu}_3)_3(\text{.mu.6-P})]$  (III) were isolated and identified. The x-ray crystal structure analyses performed on the 3 new products showed boat metal clusters for the last 2, contg. an encapsulated  $\text{P}_3^-$  ligand. I and II are triclinic, space group P.hivin.1,  $Z = 2$  and 4,  $R = 0.0362$  and  $0.0526$  and  $R' = 0.0497$  and  $0.0659$ , resp. III is monoclinic, space group P21/n,  $Z = 4$ ,  $R = 0.0589$ ,  $R' = 0.0587$ .

(FILE 'HOME' ENTERED AT 14:17:00 ON 10 OCT 1997)

FILE 'CA' ENTERED AT 14:17:08 ON 10 OCT 1997

L1           672 S METAL CARBENE  
 L2           26 S L1 AND RUTHENIUM

=&gt; s l1 and osmium

13373 OSMIUM  
 L3           8 L1 AND OSMIUM

=&gt; d 1-8 bib abs

L3   ANSWER 1 OF 8 CA COPYRIGHT 1997 ACS  
 AN   126:238816 CA  
 TI   High metathesis activity ruthenium and **osmium**  
       metal carbene complexes and their manufacture  
 IN   Grubbs, Robert H.; Schwab, Peter; Nguyen, Sonbinh T.  
 PA   California Institute of Technology, USA  
 SO   PCT Int. Appl., 40 pp.  
       CODEN: PIXXD2  
 PI   WO 9706185 A1 970220  
 DS   UG, W UZ, W VN, W AM, W AZ, W BY, W KG, W KZ, W MD, W RU, W TJ, W  
       TMEE, ES, FI, GB, GE, HU, IL, IS, JP, KE, KG, KP, KR, KZ, LK,  
       LR, LS, LT, LU, LV, MD, MG, MK, MN, MW, MX, NO, NZ, PL, PT, RO,  
       RU, SD, SE, SG, SI, SK, TJ, TM, TR, TT, UA, UG, UZ, VN, AM, AZ,  
       BY, KG, KZ, MD, RU, TJ, TM  
 RW: AT, BE, BF, BJ, CF, CG, CH, CI, CM, DE, DK, ES, FI, FR, GA, GB,  
       GR, IE, IT, LU, MC, NL, PT, SE  
 AI   WO 96-US12654 960801  
 PRAI US 95-1862 950803  
       US 95-3973 950919  
       US 96-693789 960731  
 DT   Patent  
 LA   English  
 OS   MARPAT 126:238816  
 AB   Ruthenium and **osmium** carbene compds. that are stable in  
       the presence of a variety of functional groups can be used to  
       catalyze olefin metathesis reactions on unstrained cyclic and  
       acyclic olefins. The carbene compds. are of formula XX1LL1M:CRR1,  
       where M = Os or Ru; R1 = H; R = H, (un)substituted alkyl, and  
       (un)substituted aryl; X and X1 = anionic ligand; and L and L1 =  
       neutral electron donor. The ruthenium and **osmium** carbene  
       compds. may be synthesized using diazo compds., by neutral electron  
       donor ligand exchange, by cross metathesis, using acetylene, using  
       cumulated olefins, and in a one-pot method using diazo compds. and  
       neutral electron donors. The carbene compds. may be used to  
       catalyze olefin metathesis reactions including, but not limited to  
       ROMP, RCM, depolymn. of unsatd. polymers, synthesis of telechelic  
       polymers, and olefin synthesis. Stirring a soln. of RuCl<sub>2</sub>(PPh<sub>3</sub>)<sub>3</sub> in  
       CH<sub>2</sub>Cl<sub>2</sub> at -78.degree. and treating with a soln. of  
       phenyldiazomethane in CH<sub>2</sub>Cl<sub>2</sub> at -50.degree. gave a green microcryst.  
       solid of Ru(:CHPh)Cl<sub>2</sub>(PPh<sub>3</sub>)<sub>2</sub>. The solid was used to polymerize  
       norbornene with 95-99% yield and polydispersity 1.04-1.10.

AN 125:58749 CA

TI High activity ruthenium or osmium metal carbene complexes for olefin metathesis reactions and synthesis thereof

IN Grubbs, Robert H.; Nguyen, Sonbinh T.; Johnson, Lynda K.; Hillmyer, Marc A.; Fu, Gregory C.

PA California Institute of Technology, USA

SO PCT Int. Appl., 27 pp.

CODEN: PIXXD2

PI WO 9604289 A1 960215

DS W: AM, AT, AU, BB, BG, BR, BY, CA, CH, CN, CZ, DE, DK, EE, ES, FI, GB, GE, HU, IS, JP, KE, KG, KP, KR, KZ, LK, LR, LT, LU, LV, MD, MG, MN, MW, MX, NO, NZ, PL, PT, RO, RU, SD, SE, SG, SI, SK, TJ, TM, TT

RW: AT, BE, BF, BJ, CF, CG, CH, CI, CM, DE, DK, ES, FR, GA, GB, GR, IE, IT, LU, MC, ML, MR, NE, NL, PT, SE, SN, TD, TG

AI WO 95-US9655 950728

PRAI US 94-282826 940729

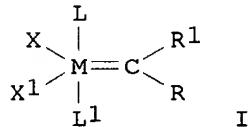
US 94-282827 940729

DT Patent

LA English

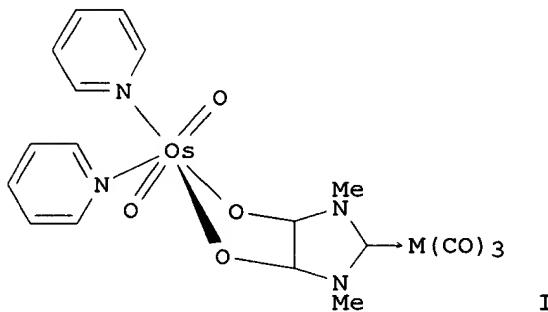
OS CASREACT 125:58749; MARPAT 125:58749

GI



AB Ru and Os carbene compds. which are stable in the presence of a variety of functional groups and which can be used to catalyze olefin metathesis reactions are discussed. Methods for synthesizing these carbene compds. are also disclosed. For example, 1.73 mmol [(cymene)RuCl<sub>2</sub>]<sub>2</sub>, 2 equiv PCy<sub>3</sub> and 1 equiv 3,3-diphenylcyclopropene react in benzene at 83-85.degree. for 6 h to give 88% Cl<sub>2</sub>Ru(:CHCH:CPH<sub>2</sub>)(PCy<sub>3</sub>)<sub>2</sub> (I). Phosphoranes, R<sub>4</sub>R<sub>5</sub>R<sub>6</sub>P:CRR<sub>1</sub>, can be used in place of cyclopropenes. Specifically, the present invention relates to carbene compds. I wherein: M is Os or Ru; R and R<sub>1</sub> are independently selected from H; C<sub>2</sub>-C<sub>20</sub> alkenyl, C<sub>2</sub>-C<sub>20</sub> alkynyl, C<sub>1</sub>-C<sub>20</sub> alkyl, aryl, C<sub>1</sub>-C<sub>20</sub> carboxylate, C<sub>2</sub>-C<sub>20</sub> alkoxy, C<sub>2</sub>-C<sub>20</sub> alkenyloxy, C<sub>2</sub>-C<sub>20</sub> alkynyloxy, aryloxy, C<sub>2</sub>-C<sub>20</sub> alkoxy carbonyl, C<sub>1</sub>-C<sub>20</sub> alkylthio, C<sub>1</sub>-C<sub>20</sub> alkylsulfonyl or C<sub>1</sub>-C<sub>20</sub> alkylsulfinyl; each optionally substituted with C<sub>1</sub>-C<sub>5</sub> alkyl, halogen, C<sub>1</sub>-C<sub>5</sub> alkoxy or with a Ph group optionally substituted with halogen, C<sub>1</sub>-C<sub>5</sub> alkyl or C<sub>1</sub>-C<sub>5</sub> alkoxy; X and X<sub>1</sub> are independently selected from any anionic ligand; and L and L<sub>1</sub> are each trialkylphosphine ligands where at least one of the alkyl groups on the phosphine is a secondary alkyl or a cycloalkyl. In a preferred embodiment, all of the alkyl groups of the trialkylphosphine are either a secondary alkyl or a cycloalkyl. In a more preferred embodiment, the alkyl groups are either iso-Pr, iso-Bu, sec-Bu, neopentyl, neophenyl, cyclopentyl or cyclohexyl. Reactions catalyzed by the above complexes include ring-opening metathesis polymn. of strained and unstrained cyclic olefins, ring closing metathesis of acyclic dienes, cross metathesis reactions involving at least one acyclic or unstrained cyclic olefin and depolymn. of olefinic polymers. For example, 0.50 mmol CH<sub>2</sub>:CHCH<sub>2</sub>OCHPhCH<sub>2</sub>CH:CH<sub>2</sub> was converted in 86% yield to the dihydropyran in benzene in the presence of I after 5 h at 20.degree.. Telechelic polymers can be prep'd. using the above complexes as catalysts.

L3 ANSWER 3 OF 8 CA COPYRIGHT 1997 ACS  
 AN 122:187782 CA  
 TI Oxy Functionalization of Metal-Coordinated Heterocyclic Carbenes  
 AU Herrmann, Wolfgang A.; Roesky, Peter W.; Elison, Martina; Artus, Georg; Oefele, Karl  
 CS Anorganisch-chemisches Institut, Technischen Universitaet Muenchen, Garching, D-85747, Germany  
 SO Organometallics (1995), 14(3), 1085-6  
 CODEN: ORGND7; ISSN: 0276-7333  
 DT Journal  
 LA English  
 OS CASREACT 122:187782; CJACS-IMAGE; CJACS  
 GI



AB Metal-coordinated 1,3-dimethylimidazolin-2-ylidene ligands undergo osmylation by **osmium** tetroxide to yield a new type of bimetallic, redox-stable complexes I (M = Cr, Mo, W) with metals in very different oxidn. states (e.g. Cr0/OsVI). This oxy functionalization does not influence the **metal-carbene** bond in a significant way (IR and NMR spectra). The single-crystal x-ray diffraction structure of I (M = Cr) was detd.

L3 ANSWER 4 OF 8 CA COPYRIGHT 1997 ACS  
 AN 120:299528 CA  
 TI Ruthenium and **osmium metal carbene** complexes for cycloolefin metathesis polymerization  
 IN Grubbs, Robert Howard; Johnson, Lynda Kaye; Nguyen, Sonbinh Thebaud  
 PA du Pont de Nemours, E. I., and Co., USA; California Institute of Technology  
 SO PCT Int. Appl., 43 pp.  
 CODEN: PIXXD2  
 PI WO 9320111 A2 931014  
 DS W: JP, KR  
 RW: AT, BE, CH, DE, DK, ES, FR, GB, GR, IE, IT, LU, MC, NL, PT, SE  
 AI WO 93-US3425 930405  
 PRAI US 92-863606 920403  
 DT Patent  
 LA English  
 OS MARPAT 120:299528  
 AB The title compds. bear Os or Ru atoms in the +2 oxidn. state and are stable in the presence of protic solvents, and are useful as high activity ring-opening metathetic catalysts for polymn. of cycloolefins. A catalyst was prep'd. by reaction of tetrakis(triphenylphosphine)ruthenium dichloride and 3,3-diphenylcyclopropene and was used to polymerize norbornene.

L3 ANSWER 5 OF 8 CA COPYRIGHT 1997 ACS  
 AN 107:134767 CA  
 TI Metathesis polymerization of exo,exo-, endo,exo- and

endo,endo-5,6-dimethylbicyclo[2.2.1]hept-2-enes; microstructure of the polymers and their hydrogenated products

AU Greene, Ruth M. E.; Ivin, Kenneth J.; McCann, G. Malachy; Rooney, John J.

CS Dep. Chem., Queen's Univ. Belfast, Belfast, BT9 5AG, UK

SO Makromol. Chem. (1987), 188(8), 1933-50

CODEN: MACEAK; ISSN: 0025-116X

DT Journal

LA English

AB Polymers of exo,exo-, endo,exo- and endo,endo-5,6-dimethylbicyclo[2.2.1]hept-2-ene monomers were prep'd. using a selection of 8 metathesis catalysts, and their structures were exam'd. by  $^{13}\text{C}$ -NMR spectroscopy. Tacticities could be detd. for the polymers of the endo,endo and endo,exo monomers and for all 3 hydrogenated polymers. RuCl<sub>3</sub> gave high-trans atactic polymers while ReCl<sub>5</sub> gave high-cis syndiotactic polymers, but WCl<sub>6</sub>/Bu<sub>4</sub>Sn gave a high-cis atactic polymer of the endo,endo monomer. The endo,exo monomer was unusual in giving polymers of relatively low cis content (fraction of cis double bonds  $\sigma$   $\approx$  0.3), and with strong exo,endo bias except in the case of RuCl<sub>3</sub>. Polymers of the exo,exo and endo,endo monomers have a blocky cis/trans double bond distribution at moderate cis content. The results were discussed in terms of a mechanism involving propagation by **metal-carbene**, **metal-carbene-olefin**, and metallacyclobutane complexes.

L3 ANSWER 6 OF 8 CA COPYRIGHT 1997 ACS

AN 106:196576 CA

TI Arene(phosphine)metal complexes. XI. Five-membered **osmium** heterocycles from alkyne insertion into an **osmium**-iodine or **osmium**-hydrogen bond

AU Werner, H.; Weinand, R.; Otto, H.

CS Inst. Anorg. Chem., Univ. Wuerzburg, Wuerzburg, D-8700, Fed. Rep. Ger.

SO J. Organomet. Chem. (1986), 307(1), 49-59

CODEN: JORCAI; ISSN: 0022-328X

DT Journal

LA German

OS CASREACT 106:196576

GI For diagram(s), see printed CA Issue.

AB The reaction of equimolar amts. of C<sub>6</sub>H<sub>6</sub>Os[P(CHMe<sub>2</sub>)<sub>3</sub>]I<sub>2</sub>, AgPF<sub>6</sub> and RC.tplbond.CCO<sub>2</sub>Me (R = H, Me, CO<sub>2</sub>Me) gives heterocycle I (X = iodo, same R). The reaction of C<sub>6</sub>H<sub>6</sub>OsH[P(CHMe<sub>2</sub>)<sub>3</sub>]I, AgPF<sub>6</sub> and HC.tplbond.CCO<sub>2</sub>Me produces I (X = R = H). The x-ray structure anal. of I (X = iodo, R = H) shows that the cation contains a 5-membered metallaheterocycle which is obtained by insertion of the alkyne into 1 of the Os-I bonds. The OsC<sub>3</sub>O ring is almost planar. The distance Os-C(1) [202(1) pm] lies between that of a Os-C single and a Os:C double bond thus indicating that for the bonding pattern of the heterocycle a resonance form with a **metal-carbene** bond must be considered.

L3 ANSWER 7 OF 8 CA COPYRIGHT 1997 ACS

AN 89:215526 CA

TI Carbene complexes. Part 15. The synthesis and properties of electron-rich olefin-derived mono- and oligo-carbenenitrosylruthenium, -**osmium** and -nickel complexes

AU Lappert, Michael F.; Pye, Peter L.

CS Sch. Mol. Sci., Univ. Sussex, Brighton, Engl.

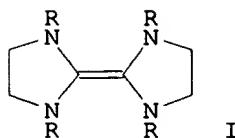
SO J. Chem. Soc., Dalton Trans. (1978), (7), 837-44

CODEN: JCDTBI; ISSN: 0300-9246

DT Journal

LA English

GI



AB  $MCl_3(NO)(PPh_3)_2$  ( $M = Ru, Os$ ),  $MCl(NO)(PPh_3)_2$  ( $M = Ru, Ni$ ), and  $Ru(NO)_2(PPh_3)_2$  reacted with the carbenes I ( $R = Me, Et, CH_2Ph$ ) to give carbenenitrosylmetal complexes, e.g.  $RuClL_2(NO)$  ( $L_2 = I, R = CH_2Ph$ ), and  $[ML_4(NO)]Cl$  ( $M = Ru, Os, R = Me$ ), which were characterized by anal. and IR and NMR spectra. Many of the complexes had complicated NMR spectra due to the inequivalence of  $N-CH_2Ph$  protons or  $N-CH_3$  groups caused by restricted rotation. The reactivities of the carbenenitrosylmetal complexes with  $Ag^+$ ,  $CO$ ,  $MeI$ ,  $I_2$ ,  $Br_2$ , and  $PhCH_2Cl$  were studied. As the metal charge increases,  $\nu(CN_2)$ , complex stability, and the barrier to  $Ru-C(carbene)$  rotation all increase,  $\delta[^{13}C(carbene)]$  becomes more shielded, and the carbene ligand increases in amidinium nature.

L3 ANSWER 8 OF 8 CA COPYRIGHT 1997 ACS

AN 84:135795 CA

TI Cyclic transition-metal carbene complexes from ring-closing reactions on the  $\pi$ -bound substrates carbon disulfide and carbon diselenide. 1,3-Dithiolan-2-ylidene and 1,3-diselenolan-2-ylidene complexes of ruthenium(II) and osmium(II)

AU Collins, T. J.; Grundy, K. R.; Roper, W. R.; Wong, S. F.

CS Dep. Chem., Univ. Auckland, Auckland, N. Z.

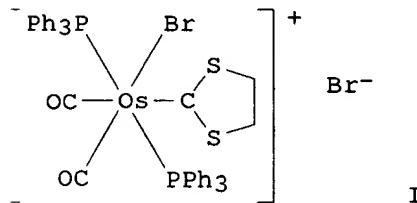
SO J. Organomet. Chem. (1976), 107(3), C37-C39

CODEN: JORCAI

DT Journal

LA English

GI



AB  $Os(CS_2)(CO)_2(PPh_3)_2$ ,  $Os(CS_2)(CO)(CNC_6H_4Me-p)(PPh_3)_2$ ,  $Ru(CS_2)(CO)(CNC_6H_4Me-p)-(PPh_3)_2$  and  $Ru(CSe_2)(CO)_2(PPh_3)_2$  react with 1,2-dibromoethane to give cationic and neutral 1,3-dithiolan-2-ylidene and 1,3-diselenolan-2-ylidene complexes (e.g. I).